UNIVERSITÉ DU QUÉBEC À MONTRÉAL

ANALYSES ISOTOPIQUES ET GÉOCHIMIQUES MENÉES SUR LES POISSONS FOSSILES ET LES SÉDIMENTS DE LA FORMATION D'ESCUMINAC (DÉVONIEN SUPÉRIEUR, MIGUASHA, QUÉBEC) ET IMPLICATIONS PALÉOENVIRONNEMENTALES

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RÉSUMÉ

Le cadre paléoenvironnemental de la Formation d'Escuminac a été investigué par le biais d'analyses géochimiques (terres rares) et isotopiques (Rb-Sr, Nd-Sm) effectuées sur du matériel fossile et des sédiments de la section type de cette formation. Pour ce faire, des échantillons d'argilite et des ichthyolithes appartenant à cinq espèces de poissons fossiles différentes (le placoderme *Bothriolepis canadensis*, l'acanthodien *Homalacanthus concinnus,* l'actinoptérygien *Cheirolepis canadensis,* le dipneuste *Scaumenacia curta* et l'ostéolépiforme *Eusthenopteron foordi*) et pour lesquels la position stratigraphique est connue ont été étudiés. Les analyses isotopiques furent réalisées en spectrométrie de masse par ionisation thermique et les abondances de terres rares ont été mesurées par ablation laser ICP-MS.

Les résultats obtenus dans cette étude suggèrent que les bioapatites ont subi un certain grade de diagénèse mais qu'il est malgré tout possible d'y récupérer des signatures paléoenvironnementales pertinentes. Le matériel dentaire apparaît plus résistant à l'altération que les os ou les écailles. Les ratios $^{87}Sr/^{86}Sr$ des bioapatites varient de 0,70804 à 0,70845. Les signatures les plus sûres sont similaires à la composition isotopique en Sr de l'eau de mer au Frasnien, suggérant un environnement marin ou saumâtre pour la Formation d'Escuminac, sans variation interspécifique ou stratigraphique claire. La majorité des échantillons analysés présentent cependant une déviation significative des valeurs marines vers un signal plus radiogénique. Cette déviation serait le résultat d'échanges post-mortem de Sr entre les fossiles et un fluide diagénétique isotopiquement distinct des eaux dans lesquelles ont vécu les poissons.

Tous les ichthyolithes sont fortement enrichis en terres rares et montrent un patron normalisé au NASC similaire à ceux décrits dans les bioapatites paléozoïques d'origine marine. Les $\varepsilon_{Nd}(T)$ des argilites varient de –4,8 à –6,4, suggérant que de jeunes sources appalachiennes ont dominé la sédimentation détritique tout au long de la mise en place de la Formation d'Escuminac. Une composition isotopique en Nd plus radiogénique (de –2,6 à –4,6) est obtenue pour les bioapatites. La divergence entre le $\varepsilon_{Nd}(T)$ des sédiments et des fossiles implique la présence d'un autre réservoir de Nd pour les ichthyolithes de la Formation d'Escuminac. Les fossiles de la Formation d'Escuminac portent une composition isotopique en Nd qui les rapproche plus de conodontes de la région baltique que des conodontes nord-américains. Un contact entre le bassin collecteur de la Formation d'Escuminac et l'océan Rhéique est ainsi proposé.

Mots clé : Escuminac, Dévonien, géochimie, paleoenvironnement, diagénèse.

INTRODUCTION

Depuis plus de 125 ans, l'assemblage fossile de la Formation d'Escuminac (Dévonien supérieur) a alimenté les études portant sur l'évolution, l'anatomie et la paléoécologie des vertébrés inférieurs, notamment au sujet de la transition cruciale entre les poissons et les tétrapodes. Cependant, en dépit de cet intérêt scientifique soutenu, aucun cadre paléoenvironnemental ne fait consensus pour la Formation d'Escuminac. Des données parfois contradictoires, provenant de la paléontologie, de la sédimentologie et de la géochimie ont conduit à une gamme d'interprétations paléoenvironnementales allant du milieu lacustre à l'environnement marin. Jusqu'à maintenant, les études géochimiques se sont concentrées sur les sédiments de la Formation d'Escuminac. Les signatures géochimiques obtenues par l'étude de roches sédimentaires étant plutôt tributaires de l'histoire géologique de ces sédiments, il est préférable d'analyser le matériel fossile si l'on souhaite obtenir des informations pertinentes sur le milieu de vie des organismes anciens. Ce travail représente la première investigation géochimique à grande échelle du matériel fossile provenant de la Formation d'Escuminac.

Ce travail vise dans un premier temps l'étude de la structure interne et de la composition en éléments majeurs des fragments de poissons fossiles utilisés dans ce projet, afin de vérifier si la minéralogie originelle est préservée. Une fois cette étape préliminaire réalisée, les analyses géochimiques et isotopiques peuvent être effectuées sur les fossiles et les sédiments de la Formation d'Escuminac. Les éléments étudiés sont le strontium (Sr), le rubidium (Rb), le samarium (Sm), le néodyme (Nd) ainsi que les autres terres rares. Ces analyses visent à renseigner sur (1) le degré de diagénèse subit par les fossiles de la Formation d'Escuminac, (2) la paléosalinité du milieu aquatique dans lequel vivait les poissons étudiés, (3) les sources sédimentaires ayant alimenté le bassin collecteur de la Formation d'Escuminac et (4) le degré de similitude entre le milieu de vie des poissons de Miguasha et d'autres masses d'eau contemporaines.

Pour réaliser ces objectifs, des échantillons d'argilite et de diverses espèces de poissons fossiles provenant de la Formation d'Escuminac ont été sélectionnés. Le choix s'est porté sur

le matériel bien conservé et pour lequel une position stratigraphique précise est connue. Une fois nettoyés des sédiments encaissants, les échantillons ont été attaqués chimiquement jusqu'à dissolution puis l'on a isolé les isotopes à l'étude (i.e., Rb, Sr, Sm, Nd) à l'aide de résines spécifiques. Ces isotopes furent analysés à l'aide d'un TIMS. Finalement, d'autres fossiles ont été étudiés au microscope électronique à balayage et au La-ICP-MS afin d'en étudier la structure et la composition en éléments majeurs et en terres rares.

La première section de ce travail présente les notions théoriques impliquées dans cette étude à propos du comportement du strontium et des terres rares. Suit une description du cadre géologique de la Formation d'Escuminac puis une présentation de la méthodologie utilisée. La quatrième section de ce mémoire exposera les résultats obtenus lors des analyses. Enfin, une interprétation paléoenvironnementale des divers résultats sera proposée.

Isotopic and geochemical analyses of fossil fish remains and shales from the Upper Devonian Escuminac Formation (Miguasha, Québec): Paleoenvironmental implications.

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Abstract- The paleoenvironmental context of the Middle Frasnian Escuminac Formation was investigated through direct geochemical (rare earth elements) and isotopic (Rb-Sr, Nd-Sm) analyses of fossil material and shales. Shale samples as well as ichthyoliths of different fish species (placoderm *Bothriolepis canadensis*, acanthodian *Homalacanthus concinnus,* actinopterygian *Cheirolepis canadensis,* dipnoan *Scaumenacia curta* and osteolepiform *Eusthenopteron foordi*) coming from the base to the top of the Escuminac Formation were analysed. The isotopic analyses were performed by thermal ionisation mass spectrometry (TIMS) and the rare earth element abundances were measured by laser ablation ICP-MS.

$^{87}Sr/^{86}Sr$ ratios for ichthyoliths vary from 0.70804 to 0.70845 and overlap with Middle Frasnian seawater Sr isotope composition, though most of the biogenic apatites analyzed show a variable drift from marine values toward a more radiogenic continental signature. This trend is possibly the result of post-mortem Sr exchange between fossils and a fluid isotopically distinct from the waters in which they developed.

All ichthyoliths are heavily enriched in rare earth elements with bell-shaped shale-normalized patterns. The $\varepsilon_{Nd}(T)$ of the shales range from –4.8 to –6.4, suggesting that a young Appalachian source dominated the detrital sedimentation for the Escuminac Formation. In contrast, more radiogenic $\varepsilon_{Nd}(T)$ values (ranging from –2.6 to –4.6) were obtained for the ichthyoliths. The discrepancy between shales and ichthyoliths $\varepsilon_{Nd}(T)$ implies the presence of a second Nd reservoir for the Escuminac bioapatites. The similarity between Nd isotope compositions of Escuminac fossils and Baltic conodonts versus North American conodonts argues for a close connection between waters of the Rheic Ocean and the Escuminac Formation collector basin.

1. INTRODUCTION

1.1. Background

The Middle Frasnian Escuminac Formation (Miguasha, Québec, Canada) is renowned for (1) the abundance, (2) the quality of preservation and (3) the phylogenetic and evolutionary importance of its fossils. Since its discovery in 1842, over 19 000 specimens have been collected from the Miguasha cliffs. The biota includes terrestrial plants, invertebrates (i.e., polychaetes, eurypterids, crustaceans, terrestrial scorpions and millipedes) as well as vertebrates. Vertebrates are represented by 20 fish species that encompass most of the Late Devonian vertebrate diversity, with the exception of chondrichthyans or cartilaginous fishes and tetrapods. The diverse ichthyofauna of the Escuminac Formation has been under scrutinity for decades, providing invaluable information on the systematic, fine anatomy and paleoecology of extinct vertebrates (Schultze and Cloutier, 1996; Arsenault et al., 2004; Burrow, 2005; Janvier et al., 2006).

Reconstructing past habitats is intricately linked to our understanding of life evolution. For instance, the environment in which the first tetrapods evolved is still disputed (Clack and Neininger, 2000) and an improved understanding of the early tetrapods habitat would allow a better conceptualization of the abiotic and biotic framework that favoured the origin of tetrapods. The Escuminac assemblage includes two taxa sharing anatomical features that link them to tetrapods, the osteolepiform *Eusthenopteron foordi* and the elpistostegalian *Elpistostege watsoni* (Cloutier and Ahlberg, 1996), with the latter being considered as the sister group of tetrapods (Schultze and Arsenault, 1985; Cloutier and Ahlberg, 1996; Schultze, 1996; Daeschler et al., 2006). Furthermore, resolving the paleoenvironmental setting of the Escuminac Formation would provide insight into factors that play a role in the formation of a Konzentrat and Konservat Lagerstätte (Parent and Cloutier, 1996) like the Escuminac Formation.

Devonian Old Red Sandstone fish assemblages have been long considered to have a freshwater origin and, by extension, so was the Escuminac assemblage (Dineley and

Williams, 1968; Brideaux and Radforth, 1970; Gray, 1988; Rust et al., 1989). However, this paradigm is disputed (Ahlberg, 1989; Schmitz et al., 1991; Schultze, 1995) and other interpretations of the depositional environment of the Escuminac Formation have been proposed: marine (Schmitz et al., 1991), coastal marine (Schultze and Arsenault, 1985; Vézina, 1991; Schultze, 1995), transitional (Chidiac, 1989 ; 1996), marine to brackish (Schultze and Cloutier, 1996 ; El Albani et al., 2002) and estuarine (Hesse and Sawh, 1992; Schultze, 1995; Cloutier et al., 1996; Maples, 1996). Among these workers, few have used geochemical parameters in their studies. Studies of the stable isotopes of C, O, and B and B concentrations (Chidiac, 1996); Na, F, Sr and La concentrations and Sr isotopes (Schmitz et al., 1991) and Mg, Ca and Fe concentrations (Vézina, 1991) are all suggestive of a marine influence for the Escuminac Formation (El Albani et al., 2002). With the exception of Schmitz et al. (1991) who used a single bony fragment, all the remaining geochemical studies were performed on the sediments rather than on bioapatites. The goal of this paper is to address this paleoenvironmental debate through a broader geochemical (rare earth elements) and isotopic (Sr and Nd) study of fossil fish remains and the enclosing sediments of the Escuminac Formation.

1.2. Preservation of pristine Sr isotope signatures in bioapatites

^{87}Sr is produced by the radioactive decay of ^{87}Rb, which is generally highly abundant in continental rocks. This means that water from lakes and rivers will normally have higher, more radiogenic, $^{87}Sr/^{86}Sr$ ratios that reflect the age and Rb/Sr ratio of the bedrock in the drainage basin, than seawater (Schmitz et al., 1991). In addition, because the residence time of Sr in seawater (4-5 Ma) exceeds the mixing time of ocean water ($\sim 10^3$ years), oceans have a uniform Sr isotopic composition at a given time (Dasch and Campbell, 1970). For instance, the present-day world's oceans possess a homogenous $^{87}Sr/^{86}Sr$ ratio of 0.7092 (De Paolo and Ingram, 1985), whereas continental waters have higher and more variable $^{87}Sr/^{86}Sr$ ratios, ranging from ~0.710 to ~0.730 (Veizer and Compston, 1974; Palmer and Edmond, 1989).

The Sr concentration is also different between seawater and freshwater: Sr in seawater is generally two orders of magnitude greater than in freshwater (Bryant et al., 1995; Holmden et al., 1997). This large difference leads to difficulties in identifying between mixtures of seawater and freshwater because even in brackish environments, the freshwater $^{87}Sr/^{86}Sr$ signature is often completely overwhelmed by the saltwater signal (Veizer and Compston, 1974; Holmden et al., 1997; Kohn and Cerling, 2002; Holmden and Hudson, 2003).

In paleoenvironmental investigations, the $^{87}Sr/^{86}Sr$ ratio of calcitic and phosphatic biomineralization can be used as a proxy for the seawater composition because Sr^{2+} easily substitutes for Ca^{2+} in biogenic calcite and apatite owing to their similar ionic radii. Moreover, it is well established that Sr is incorporated *in vivo* in biomineralization without significant fractionation (Dasch and Campbell, 1970; Schmitz et al., 1991; Koch et al., 1992; Kaufman et al., 1993), thus recording the Sr-isotopic composition of the environment in which the animal is living (Shaw and Wasserburg, 1985; Staudigel et al., 1985). A crucial issue, however, is whether the original signal is preserved after the death of the animal (Schmitz et al., 1997). The case of bioapatites is relevant. Ichthyoliths (i.e., small fish remains such as isolated bones, teeth, scales) and conodont elements (i.e., small feeding apparatus of an extinct group of jawless chordates) share a common general mineralogy, a carbonated form of hydroxyapatite [$Ca_{10}(CO_3,PO_4)_6(OH)_2$; Trueman and Tuross, 2002]. This calcium phosphate is thermodynamically unstable and during burial and diagenesis, it may be wholly or partially altered. During the process of fossilization, the organic components are lost, increasing the porosity within bioapatites and simultaneously, authigenic minerals precipitate, either in intercrystalline spaces or in larger vascular spaces (permineralization), thus increasing bioapatite density (Trueman and Tuross, 2002). It is this increase in density that gives stability and stops further exchange between biominerals and their environment (Trueman and Tuross, 2002). During these processes, trace elements are either removed or added (e.g., Sr) in the bioapatite (Nelson et al. 1986; Barrat et al., 2000). These processes lead to the introduction of secondary Sr and a rapid increase in Sr content during early diagenesis (Schmitz et al., 1991) by up to several thousand ppm in fossil apatite (Staudigel et al., 1985; Grandjean et al., 1987; Schmitz et al., 1991). Several authors have proposed that these exchanges can drastically alter biological and environmental signals recorded *in vivo*

(Nelson et al., 1986; Bertram et al., 1992; Holmden et al., 1996, Dufour et al., 2007). On the other hand, other workers (Shaw and Wasserburg, 1985; Staudigel et al., 1985, Holmden et al., 1996) suggest that preservation of the original paleoenvironmental signature is possible; if the bioapatite exchanged little Sr with its burial environment or if it happened when pore fluids were still in contact with waters in which the organism was living.

In their broad study, Schmitz et al. (1991) analysed the $^{87}Sr/^{86}Sr$ ratio of placoderm material (*Bothriolepis canadensis*) from the Escuminac Formation. However, their analyses were conducted on a single bony fragment and they believed that the specimen may have been diagenetically altered. For these reasons they recommended further geochemical investigations of the Escuminac Formation fauna. Other studies focusing on the sediments of the Escuminac Formation have also indicated that the Escuminac Formation is diagenetically altered (Chidiac, 1989; Hesse and Sawh, 1992; El Albani et al., 2002). However, there is no unequivocal consensus on the degree of alteration, with El Albani et al. (2002) suggesting a lower level than Chidiac (1989) and Hesse and Sawh (1992).

1.3. Preservation of pristine rare earth elements abundances in bioapatites

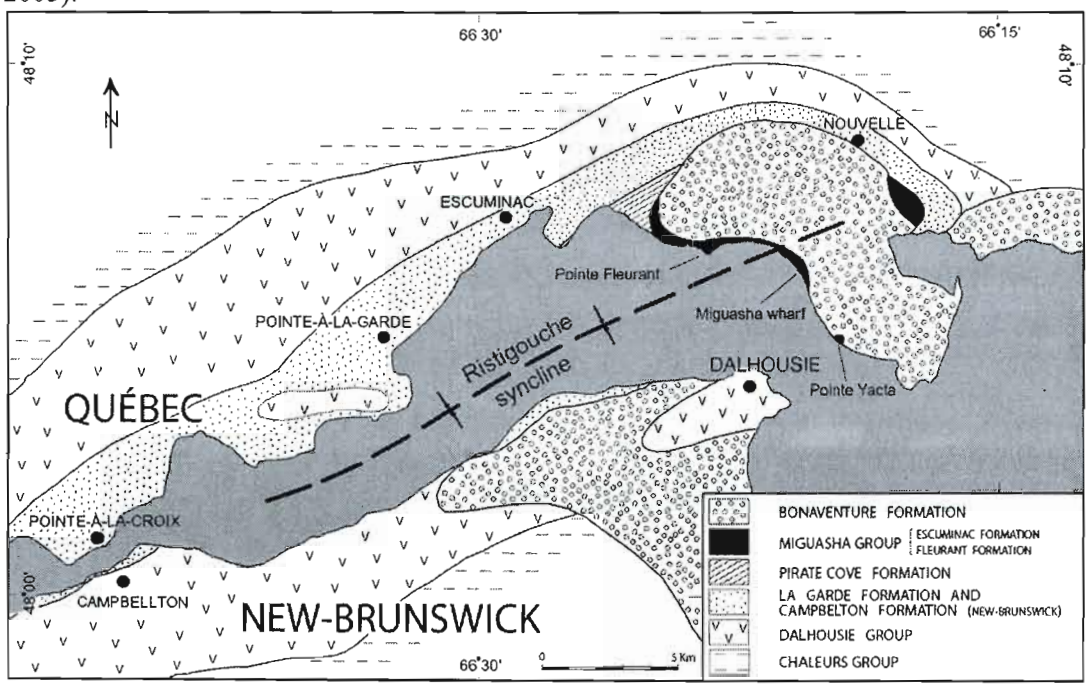
No vital role is known for the rare earth elements (REE) and they are thus found in very low concentrations *in vivo* (Trueman, 1999). However, studies have shown that there is a spectacular *post mortem* enrichment of these elements in both recent and ancient bioapatites. Like Sr, the substitution occurs in the Ca site of apatite. This drastic diagenetic enrichment, up to 10^3-10^6 time their initial concentration in ichthyoliths and conodonts (Wright et al., 1984; Shaw and Wasserburg, 1985; Holmden et al., 1996), will normally swamp any signal recorded during the life of the animal. However, it has been noted that the incorporation happens very quickly, near the water-sediment interface, in modern fish apatite (Staudigel et al., 1985; Elderfield and Pagett, 1986; Wright et al., 1987; Martin and Haley, 2000). If the bioapatites do not reach equilibrium with pore waters during their burial history (Martin and Haley, 2000), the REE characteristics of bottom water or early diagenetic environment can then be recovered (Wright et al., 1984; Staudigel et al., 1985; Keto and Jacobsen, 1987;

Wright et al., 1987; Trueman and Tuross, 2002) giving insights on the evolution of marine REE patterns over geological time (Grandjean et al., 1987; Wright et al., 1987; Grandjean-Lécuyer et al., 1993), the redox state of ancient seawater (Wright et al., 1984; Elderfield and Pagett, 1986; Holser, 1997; Picard et al., 2002; Kemp and Trueman, 2003) and the provenance of the sediments (Wright, 1995). On the other hand, some studies tend to demonstrate that late diagenetic processes could alter the original signature (Elderfield and Pagett, 1986; Sholkovitz et al., 1989; Toyoda and Tokonami, 1990; Holmden et al., 1996).

2. GEOLOGICAL SETTING

The Escuminac Formation is situated on the south coast of the Gaspé Peninsula, Québec (Fig. 1). The main outcrops are located in the locality of Miguasha, along the Restigouche River estuary but, recently, new outcrops have been discovered as much as 40 km inland from the type section in Miguasha. The type section of the Escuminac Formation is 119 m thick (Sawh, 1982) and is exposed along cliffs that range from 3 to 30 m in height. The Escuminac Formation conformably overlies the Fleurant Formation, a conglomerate with sandstone lenses interpreted as proximal alluvial deposits of early Late Devonian age (Rust et al., 1989). Together, these two formations form the Miguasha Group (Dineley and Williams, 1968).

Figure 1. Simplified geological map of the Miguasha area (modified from Desbiens et al., 2005).



The Escuminac Formation is overlain along an angular unconformity by the Mississippian Bonaventure Formation that is composed of alternating conglomerate and coarse sandstone (Desbiens et al., 2005). A middle Frasnian (Upper Devonian) age has been assigned to the Escuminac Formation, based on its miosporal content and fish assemblage (Cloutier et al., 1996). The main lithologies of the Escuminac Formation are, in decreasing order of abundance: shale, sandstone, siltstone, laminite and conglomerate. The laminite lithofacies consists of alternating dark (clay and organic matter) and light (silt-size calcite and quartz) laminae. This siliciclastic lithofacies has been interpreted as tidal-controlled deposits (Cloutier et al., in prep.). Leduc and Belles-Isles (1989) divided the formation into 394 beds of variable thickness, corresponding to major successive lithological changes. The base of the formation (beds 1-7), corresponds to a shallow water littoral environment subjected to episodic aerial exposures (Desbiens et al., 2005). The fish remains first appear in bed 8 and continue to the upper limit of the formation, although their distribution is uneven throughout the stratigraphic sequence (Cloutier et al., 1996). Fibrous calcite and carbonate concretions are also found at different levels and are interpreted to be of early diagenetic origin (El Albani et al., 2002). This is supported by the fact that concretions frequently contain well-preserved, articulated remains, indicating that carbonate cementation began early and was completed before decay of the organic parts could occur (Canfield and Raiswell, 1991a). Numerous lines of evidence suggest that anoxic/hypoxic conditions prevailed at the water-sediment interface and in the sediment at different periods of deposition of the Escuminac Formation, mainly when laminated lithofacies were formed (Cloutier et al., in prep). The evidence includes; (1) the abundance of concretions and pyrite (Canfield and Raiswell, 1991a, 1991b), (2) the absence of bioturbation, (3) the excellent state of preservation of the fish remains (Canfield and Raiswell, 1991b), (4) the poor diversity of the benthic assemblage, (5) lack of evidence of macrophagous or scavenger activity, and (6) the repetitiveness of acanthodian mass mortality events.

3. MATERIAL AND METHODS

3.1. Sampling

All specimens were collected in the type section of the Escuminac Formation during the summer 2006. Emphasis was given on material for which a precise stratigraphic position was known in order to investigate potential temporal variations of different geochemical signatures during the sedimentation in the collector basin of the Escuminac Formation. When available, complete tooth material was used preferentially; if not, tooth fragments, bones or scales were picked. Bones and dentine have smaller crystal size (greater surface area for exchange) and higher organic content than enamel (Trueman and Tuross, 2002). For these reasons, enamel is considered more resistant to diagenetic overprinting than bone and dentine (Elliott, 2002). However, tooth enamel from the Miguasha teeth was frequently too thin to provide sufficient sample for analyses, thus whole teeth were analysed. Ichthyoliths were mechanically isolated and cleaned of detrital sediments and diagenetic calcite under binocular microscope using stainless steel instruments and 5% acetic acid. Samples were subsequently boiled in methanol in order to remove any traces of recent organic contaminants.

3.2. Scanning electron microscopy (SEM) and Laser ablation – inductively coupled plasma - mass spectrometry (LA-ICP-MS)

As a preliminary characterization, three teeth from the osteolepiform *Eusthenopteron foordi* and one dermal bone plate from the placoderm *Bothriolepis canadensis* were mounted in epoxy resin in preparation for scanning electron microscopy, X-ray mapping and REE analysis by laser ablation ICP-MS. X-ray mapping and electron microscope photographs were obtained using energy dispersive X-ray (EDX) analyses coupled to a Hitachi S-4300SE/N variable pressure – scanning electron microscope at Université du Québec à Montréal. The REE analyses were conducted at McGill University with a New-Wave UP-213 Laser Ablation System coupled to a PerkinElmer/SCIEX ELAN 6100 DRCplus ICP-MS. REE data in the fossil material were normalized against the Ca content of hydroxyapatite that

forms the bone and tooth structures and repeated measurements of REE in the NIST-610 glass standard yielded average errors that were less than 10% relative standard deviation.

3.3. Strontium, neodymium and samarium isotope analyses

The rest of the fossil material (n = 34), along with the shale samples (n = 6), was used for Sr, Nd and Sm measurements by thermal ionization mass spectrometry (TIMS). The preparation of these samples was performed under clean room conditions. Specimens of the two main species involved in this study (*Bothriolepis canadensis* and *Eusthenopteron foordi*) were selected to represent seven stratigraphic levels: (1) Beds 8-10; (2) 23-28; (3) 39-46; (4) 214-219; (5) 272; (6) 351; (7) 390. In addition, fragments of three additional fish species (the acanthodian *Homalacanthus concinnus,* the actinopterygian *Cheirolepis canadensis* and the dipnoan *Scaumenacia curta*), were collected either from level (1) or (6) to investigate possible interspecific variation in the Sr isotopic ratio.

After cleaning, approximately 20 mg of each sample was weighed, some of which were spiked with a ^{87}Rb-^{84}Sr tracer solution (spike) to determine Rb and Sr concentrations by isotope dilution and all samples were spiked with a ^{149}Sm-^{150}Nd solution to determine Nd and Sm concentrations and correction for production of ^{143}Nd since the time of deposition. Samples were subsequently dissolved in Savillex™ beakers using 3 M HNO_3. After evaporation at about 130°C, dry residues were taken up with 1 ml of 3 M HNO_3 and then centrifuged. The resulting solution was passed through a Sr specific resin (Eichrom© Sr-spec-resin) to isolate the Sr fraction. The rinse from this column was collected and evaporated in preparation for isolating the REE fraction. The REE were concentrated by passing the remaining samples through Eichrom© TRU-spec-resin followed by separation of Nd and Sm using Eichrom© Ln-spec-resin. The $^{87}Sr/^{86}Sr$ ratio of diagenetic calcite was also investigated using a bony plate from *Bothriolepis canadensis* in which the median cancellous bone layer was filled with calcite crystals. The bony plate was immersed in 0.1 M HNO_3 for 30 minutes, allowing the calcite to partially dissolve, while leaving the bone structure intact. The solution was then removed, centrifuged and the Sr fraction was isolated as described above. For

comparison, three other samples from the same specimen were collected and leached for 60 minutes (0.1 M HNO_3), 180 minutes and finally until complete dissolution in HCl and HF. Again, the Sr fraction was separated by the method described above. Finally, Nd and Sm isotope compositions were determined on shale samples from the same stratigraphic levels used for the fossils, with the exception of level (2). After being crushed, approximately 0.1 g of the powdered shale was spiked with a mixed Sm-Nd tracer and dissolved in a Teflon bomb with 14 M HNO_3 and concentrated HF over a period of 5-7 days at 150°C. The resulting solution was evaporated, then redissolved in a small amount of perchloric acid ($HClO_4$) and evaporated once more in order to convert fluoride salts to chloride salts. The samples were then taken up in 6N HCl and fluxed overnight to ensure dissolution. The solution was then loaded on a column with anion exchange resin (AG1-X8) in order to remove Fe and then the REE and Sm and Nd were concentrated using the procedures described above.

All isotopic measurements were conducted on a VG SECTOR 54 mass spectrometer at the Université du Québec à Montréal. The Sr fractions were loaded onto a single Re filament in a phosphoric acid – tantalum oxide solution and measured in static mode. Replicate analyses of the Sr standard NBS987 yielded a value of 0.710241 ± 18 (2σ, n = 6). The Sm and Nd fractions were loaded onto Ta side filaments and measured as a triple filament array with a Re center filament. Sm was analysed in static mode and Nd was measured in dynamic mode. Replicate analyses of the Nd standard JNdi-1 yielded a value of 0.512153 ± 11 (2σ, n = 10) during the period of this study. This value is higher than the accepted value of 0.512115 ± 7 for JNdi-1 (Tanaka et al., 2000) and thus all Nd analyses were normalized to this accepted value.

4. RESULTS

4.1. X-ray maps

The results of scanning electron microscopy of representative *Bothriolepis canadensis* and *Eusthenopteron foordi* biomineralizations used in this study are given in Figure 2 and Table 1. Figure 2 shows X-ray maps for Ca and P for each specimen produced by energy dispersive (EDX) analyses with the percent abundances for the elements given in Table 1 along with the Ca/P ratios. The abundance of Ca and P in both specimens is consistent with the calcium phosphate/apatite composition of fossil bone and tooth material. The X-ray mapping reveals the bony structure of the cancellous bone layer of *Bothriolepis* plate (Fig. 2a, b) in which calcium is found in both the bony wall (the bone trabeculae; Burrow, 2005) and the spaces and phosphorus is concentrated in bone trabeculae. This suggests that the bone trabeculae are composed of apatite while the spaces are filled with calcite.

The pulp cavity of the tooth of *Eusthenopteron foordi* is also filled with secondary calcite (Fig. 2c). Both calcium and phosphorus are found in the dentine and enamel of the tooth (Fig. 2c, d) with Ca/P ratios (~ 2) indicative of stoichiometric apatite and comparable to Ca/P values of Ordovician conodonts (Holmden et al., 1996) and teeth (Weatherell and Robinson, 1973).

Figure 2. X-ray maps of ichthyoliths from the Escuminac Formation. Calcium and phosphorus distribution in the cancellous bone layer of *Bothriolepis canadensis* (a and b) and in tooth of *Eusthenopteron foordi* (c and d). bt, bone trabeculae; d, dentine; e, enamel; pc, pulp cavity; s, space; c, calcite.

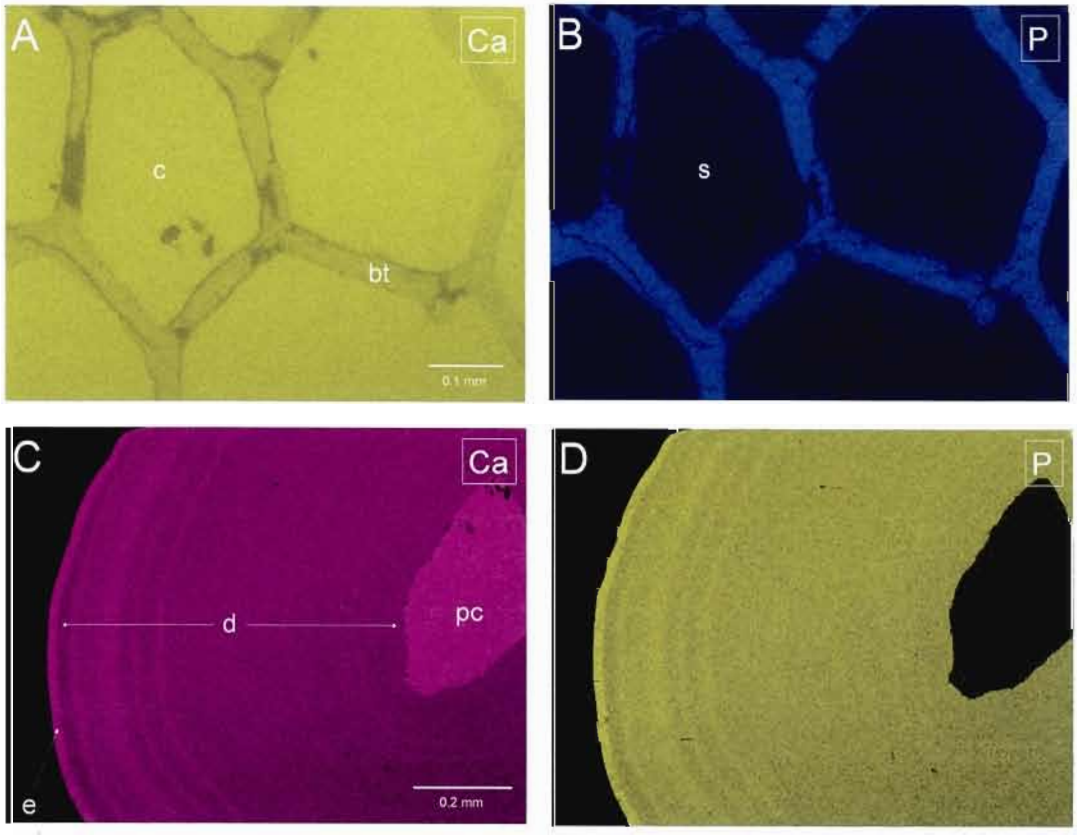


Table 1. Major element composition of fish tooth enamel, dentine and conodont crown and basal body.

Material	Ca (wt%)	P (wt%)	Ca/P
This study (2008)			
Enamel site 1	38.8	19.4	2.0
Dentine site 1	32.0	14.4	2.22
Weatherell and Robinson (1973)			
Enamel	37.6	18.3	2.05
Dentine	40.3	18.6	2.17
Holmden et al. (1996)			
Conodont crown	37.6	17.7	2.12
Conodont basal body	33.0	13.9	2.37

Studies of hydroxyapatite in fossil bone and fish teeth indicate that Ca/P ratios vary between 1.67 and 2.2 and that ratios above or below these values are either altered or contain admixtures of secondary minerals (quartz, calcite; Nemliher et al., 2004). These values argue in favour of preservation of the apatitic composition of both bone and tooth from the Escuminac Formation with addition of diagenetic calcite in pore spaces. The banded pattern evident in the tooth (Fig. 2c, d) likely reflects the growth of dental tissue.

4.2. Sr in bioapatites

The $^{87}Sr/^{86}Sr$ ratio along with selected Sr concentrations for *Bothriolepis canadensis*, *Homalacanthus concinnus*, *Cheirolepis canadensis*, *Scaumenacia curta*, *Eusthenopteron foordi* and diagenetic calcite are given in Table 2. Stratigraphic variation of $^{87}Sr/^{86}Sr$ for five fish species and for different types of material are shown respectively in Figure 3 and Figure 4. Individual samples are shown in Figure 4, whereas Figure 3 depicts, where possible, the average of values obtained for the same species in a single bed. This explains the greater dispersion of values seen in Fig. 4.

Table 2. Sr isotope measurements of Miguasha bioapatites and diagenetic calcite.

Sample name	Material	Bed	Height[a]	Sr (ppm)	$^{87}Sr/^{86}Sr$ (2σ)
		Bothriolepis canadensis			
Bot 8A	bone	8	5.1	1650	0.70829 (2)
Bot 10A	bone	10	6.2	/	0.70834 (2)
Bot 24A	bone	24	10.0	/	0.70832 (3)
Bot 26,5A	bone	26	10.3	/	0.70839 (2)
Bot 36A	bone	36	13.7	/	0.70830 (2)
Bot 39A	bone	39	15.0	/	0.70836 (2)
Bot 218A	bone	218	53.8	2389	0.70834 (2)
Bot 219A	bone	219	54.6		0.70831 (2)
Bot 272A	bone	272	67.5	3217	0.70823 (2)
Bot 272B	bone	272	67.5	/	0.70831 (2)
Bot 351 (133)A	bone	351	87.2	/	0.70827 (2)
Bot 351 (133)B	bone	351	87.2	2751	0.70829 (2)
Bot 386-394A	bone	390	114.7	/	0.70829 (2)
Bot stensioA	bone	390	114.7	2310	0.70839 (2)
		Eusthenopteron foordi			
Eus 8B	tooth	8	5.1	1771	0.70815 (1)
Dent 4	tooth	8	5.1	2913	0.70830 (2)
Eus 23A	tooth	23	9.8	/	0.70830 (2)
Eus 28A	tooth	28	10.6	/	0.70833 (2)
Dent 5	tooth	44	15.8	2095	0.70821 (2)
Eus 46A	tooth	46	17.1	2471	0.70804 (1)
Eus 214A	bone	214	51.9	3696	0.70829 (2)
Eus 214B	bone	214	51.9	/	0.70845 (2)
Dent 3	tooth	272	67.5	2328	0.70815 (2)
Eus 351 (165)A	tooth	351	86.8	/	0.70825 (2)
Eus 351 (133)A	bone	351	87.2	/	0.70827 (2)
Eus stensioA	bone	390	114.7	/	0.70829 (2)
Eus stensioB	bone	390	114.7	/	0.70832 (2)

Dent 6	tooth	unknown	unknown	2760	0.70827 (1)
		Cheirolepis canadensis			
Che 8A	bone	8	5.1	/	0.70823 (1)
Che 8B	bone	8	5.1	/	0.70824 (2)
		Homalacanthus concinnus			
Hom 8A	scales	8	5.1	/	0.70825 (2)
Hom 8B	bone	8	5.1	/	0.70842 (2)
		Scaumenacia curta			
Scau 351 (165)A	bone	351	86.8	/	0.70830 (2)
Scau 351B	bone	351	86.8	/	0.70829 (2)
		Authigenic calcite			
Bot218 calc1	authigenic calcite	218	53.8	/	0.70831 (2)
Bot218 calc2	authigenic calcite	218	53.8	/	0.70830 (2)
Bot218 calc3	authigenic calcite	218	53.8	/	0.70826 (2)
Bot218 calc4	authigenic calcite	218	53.8	/	0.70832 (2)

(a) Height (in meters) based on the stratigraphic column of Sawh (1982).
(/) Not measured.

Figure 3. $^{87}Sr/^{86}Sr$ variation for fish material and diagenetic calcite from the Escuminac Formation. The grey area shows the amplitude of variation of seawater $^{87}Sr/^{86}Sr$ for the Middle Frasnian (Veizer et al., 1999) and the arrow is pointing toward freshwater values. The scale bar represents average 2σ.

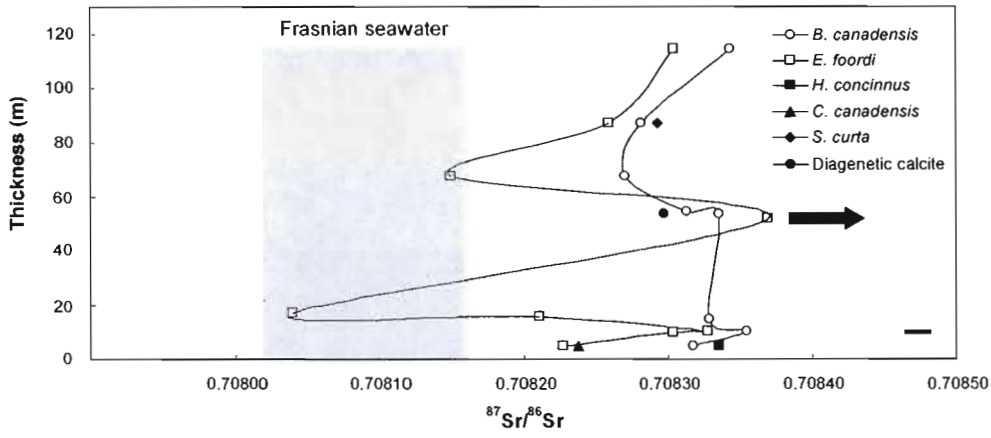
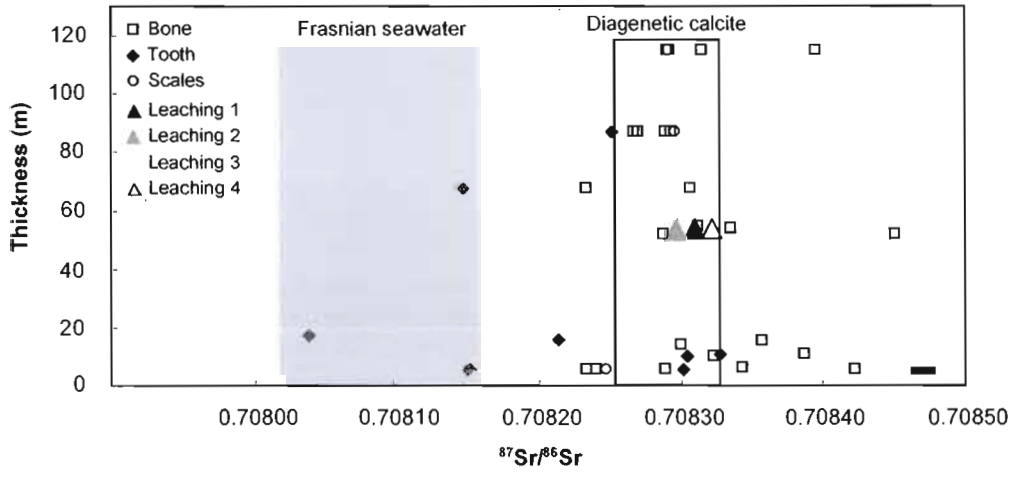
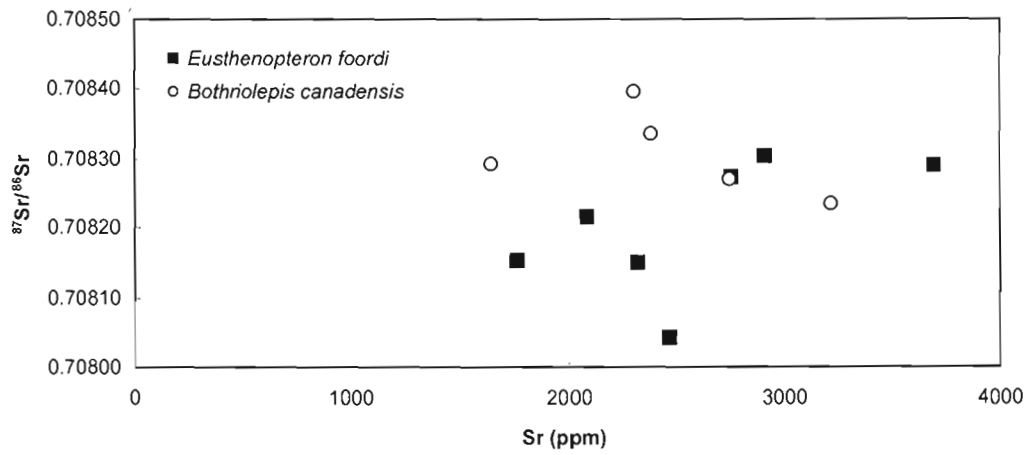


Figure 4. $^{87}Sr/^{86}Sr$ variation by tissue type and calcite leaching experiment. The grey area shows the amplitude of variation of seawater $^{87}Sr/^{86}Sr$ for the Middle Frasnian (Veizer et al., 1999) while the white area encompasses the values obtained for diagenetic calcite used in this study. "Leaching 1-4" refers to progressive leaching of diagenetic calcite, from initial immersion in 0.1 M HNO_3 ("Leaching 1") to complete dissolution in HCl and HF ("Leaching 4"). The scale bar represents average 2σ.



The overall $^{87}Sr/^{86}Sr$ variation ranges from 0.70804 to 0.70845. *Eusthenopteron* teeth are the only fossil material to fall within or near Frasnian seawater values (Fig. 3, 4). All other species and materials fall above seawater values. The $^{87}Sr/^{86}Sr$ of *Bothriolepis canadensis* bone is similar to the ratio measured by Schmitz et al. (1991) for a single plate from the Escuminac Formation (0.708382). The diagenetic calcite values indicate that the first leach of the calcite is radiogenic (0.70831), whereas subsequent leaches are less radiogenic (0.70825-0.70829). The final dissolution ("Leaching 4") of the calcite returns to a radiogenic value similar to the initial leach (0.70832). Figure 5 shows $^{87}Sr/^{86}Sr$ ratios compared with Sr concentrations in representative samples of *Bothriolepis canadensis* and *Eusthenopteron foordi*. There is no consistent trend between $^{87}Sr/^{86}Sr$ and Sr concentration. This likely reflects disturbance of the Sr isotope system owing to addition of Sr from diagenetic fluids.

Figure 5. Covariation between $^{87}Sr/^{86}Sr$ and Sr concentration for *Bothriolepis canadensis* and *Eusthenopteron foordi*.



4.3. REE in bioapatites and diagenetic calcite

The REE concentrations in ichthyoliths and diagenetic calcite are given in Table 3. REE profiles for *Eusthenopteron* teeth, *Bothriolepis* plates and diagenetic calcite are shown in Figure 6. The REE abundances are normalized against the North American Shale Composite (NASC). The profiles for the fossil material form a distinctive bell-shaped pattern found in many marine bioapatites (Wright et al., 1984; Grandjean et al., 1987; Wright et al., 1987; Bertram et al., 1992; Reynard et al., 1999; Kemp and Trueman, 2003). The REE profile of the diagenetic calcite is relatively flat and 1-2 orders of magnitude less enriched than the bioapatites. There is no correlation between REE content and stratigraphic position within the Escuminac Formation.

Figure 6. Comparison of shale-normalized (NASC) REE concentrations between ichthyoliths and authigenic calcite from the Escuminac Formation.

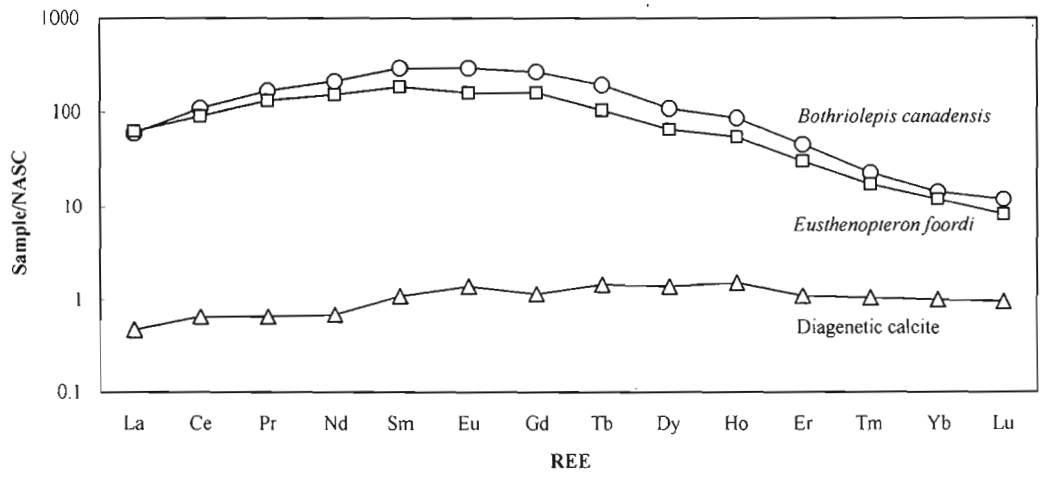


Table 3. REE abundances (ppm) for Miguasha fossil material and authigenic calcite.

Sample name	Species	Material	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Dent 2	*E. foordi*	tooth	2383	10474	1609	7859	1591	342	1123	119	475	69	117	10	41	5
Dent 7	*E. foordi*	tooth	1583	7350	1320	7389	1935	382	1646	183	723	98	153	11	42	4
Dent 8	*E. foordi*	tooth	2039	6876	1035	5093	1041	198	828	92	394	58	103	9	36	4
Bot-apatite	*B. canadensis*	bone	1895	8272	1321	6985	1718	366	1426	163	656	93	154	11	45	6
Bot-calcite	*B. canadensis*	authigenic calcite	15	47	5	23	6	2	6	1	8	2	4	1	3	0

4.4. Sm-Nd in bioapatites and shales

The results for the Sm-Nd analyses of representative *Eusthenopteron* teeth and bone and *Bothriolepis* plates from different stratigraphic levels are given in Table 4 along with analyses of sediments (shales/siltstones) from the same level. The Sm and Nd concentrations in the fossil material range from 800 to 1800 ppm and 4000 to 7100 ppm, respectively. These concentrations are consistent with those determined by LA-ICP-MS (Table 3). The $^{147}Sm/^{144}Nd$ ratios range from 0.117 to 0.164 and initial ε_{Nd} values (at 380 Ma; Gradstein et al., 2004) range between -2.6 and -4.6. The host sediments have Sm (5-8 ppm) and Nd (26-37 ppm) concentrations and $^{147}Sm/^{144}Nd$ ratios (0.123-0.136) typical of crustal rocks (Taylor and McLennan, 1985). The initial ε_{Nd} values of the sediments range between -4.8 to -6.4 and are lower than ε_{Nd} values of the fossil material.

Table 4. Sm-Nd isotope data for Miguasha shales and fossil material.

Sample name	Material	Bed	Height[a]	Nd (ppm)	Sm (ppm)	$^{147}Nd/^{144}Nd$	$^{143}Nd/^{144}Nd$ (2σ)	$\varepsilon_{Nd}(T)$[b]	T_{DM}[c]
				Bothriolepis canadensis					
Bot 8A	bone	8	5.1	4206	846	0.1216	0.512240 (9)	-4.1	1.5
Bot 39A	bone	39	15.0	5563	1080	0.1174	0.512284 (14)	-3.1	1.4
Bot 218A	bone	218	53.8	5022	1174	0.1413	0.512304 (8)	-3.8	1.8
Bot 272A	bone	272	67.5	4617	1225	0.1604	0.512373 (8)	-3.4	2.2
Bot 351(133)A	bone	351	87.2	5720	1507	0.1593	0.512413 (13)	-2.6	2.1
Bot 386-394A	bone	390	114.7	6636	1793	0.1633	0.512369 (12)	-3.6	2.4
				Eusthenopteron foordi					
Eus 8B	tooth	8	5.1	4021	823	0.1237	0.512219 (9)	-4.6	1.6
Eus 46A	tooth	46	17.1	7099	1649	0.1404	0.512264 (26)	-4.6	1.8
Eus 214B	bone	214	51.9	5506	1152	0.1265	0.512243 (10)	-4.3	1.6
Eus 351(133)A	bone	351	87.2	6279	1701	0.1638	0.512369 (10)	-3.7	2.4
Eus stensioA	bone	390	114.7	6479	1744	0.1627	0.512407 (12)	-2.9	2.2
				Shales					
Shale 8.8	shale	8	5.1	26	5	0.1233	0.512126 (10)	-6.4	1.7
Shale 46.8	shale	46	17.1	29	6	0.1257	0.512191 (9)	-5.3	1.7
Shale 219.4	shale	219	54.6	35	7	0.1283	0.512183 (11)	-5.6	1.7
Shale 272.1A	shale	272	67.5	36	8	0.1357	0.512242 (13)	-4.8	1.8
Shale 351(165)	shale	351	86.8	30	6	0.1224	0.512131 (9)	-6.3	1.7
Shale 393	shale	393	116.6	37	8	0.1291	0.512185 (7)	-5.6	1.7

(a) Height (in meters) based on the stratigraphic column of Sawh (1982).
(b) Age for εNd(T) calculation is 380 Ma.
(c) Depleted mantle model ages (TDM) calculated assuming a linear depleted mantle after Jacobsen (1988).

5. DISCUSSION

5.1. Diagenetic and paleoenvironmental considerations for Sr in ichthyoliths

The high Sr content measured in the bioapatites from the Escuminac Formation indicate that there has been significant post-mortem uptake of this element (Nelson et al. 1986). The question is whether this uptake has altered the original isotopic signatures of the fossil material. For the same stratigraphic level, different ichthyoliths carry different Sr isotope compositions (Fig. 3). There are two potential explanations: different ratios reflect (1) different signatures recorded originally in vivo (and thus different environments exploited by the fish species), or either (2) different degrees of diagenetic alteration of the pristine signature. For many reasons, the second hypothesis is more plausible. Firstly, the lowest ratios are found in teeth (Fig. 4), a material considered less prone to post-mortem alteration (Trueman and Tuross, 2002). Secondly, many other biogenic samples used in the present study have $^{87}Sr/^{86}Sr$ ratios equivalent to, or even more radiogenic than calcite formed under diagenetic conditions. Thirdly, biogenic apatites that belong to the same species and coming from the same bed sometimes carry strongly different $^{87}Sr/^{86}Sr$ (e.g., *Eusthenopteron foordi* in bed 8). These results suggest that the majority of specimens used in this study have experienced diagenesis to a certain extent. This alteration is likely owing to post-mortem interaction between ichthyoliths and a fluid isotopically distinct from the waters in which they developed. As noted by Martin and Scher (2004), the deviation is normally toward more radiogenic values when the biogenic apatites are hosted by silicate rocks. The Miguasha samples are consistent with this model. The lowest $^{87}Sr/^{86}Sr$ are found in the *Eusthenopteron* teeth. This likely reflects the fact that the teeth are overall less porous than bone (Trueman and Tuross, 2002) and infilling of the pore spaces by sediments and diagenetic calcite would lead to higher $^{87}Sr/^{86}Sr$ ratios. Slightly higher $^{87}Sr/^{86}Sr$ ratios in the other bioapatites might be due to the presence of trace amounts of sediments and calcite in the pore spaces or to a greater interaction with pore waters. Given that the lowest values, considered more reliable, overlap the Frasnian seawater Sr composition and that most of the Sr isotopic variation is close to seawater values, a marine influence cannot be discounted and may be more likely, suggesting a brackish to marine environment for the Escuminac Formation. In comparing the

Sr concentrations and $^{87}Sr/^{86}Sr$ ratios, there is no clearly defined trend that would indicate mixing of fresh and saltwater (Fig. 5). Owing to the variable degree of diagenesis experienced by the ichthyoliths used in this study, it is risky to conclude on any interspecific or stratigraphic variation of the Sr composition.

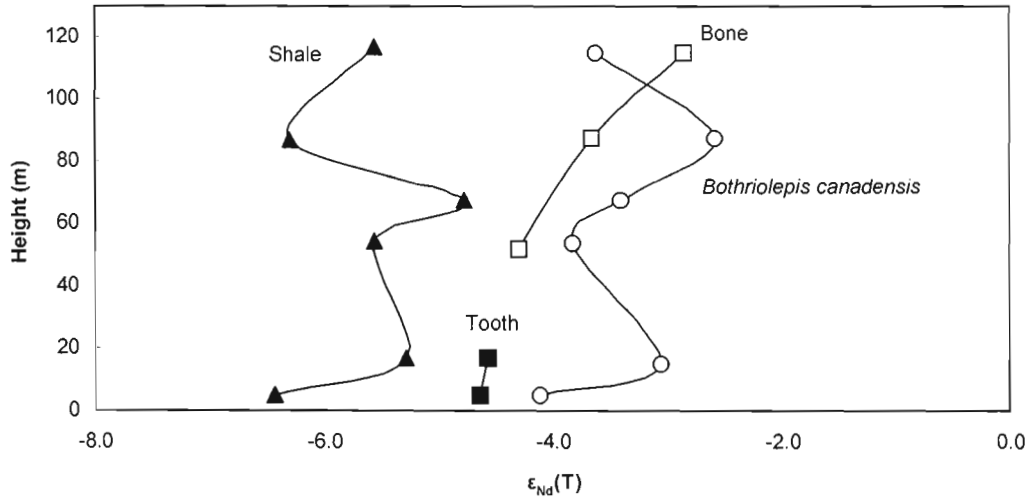
5.2. Diagenetic considerations for REE in ichthyoliths

The high REE contents of the bone and teeth material reflect the uptake of REE during diagenesis (Wright et al., 1984; Shaw and Wasserburg, 1985). Again, the question is whether this uptake has altered the original ε_{Nd} value. The bell-shaped profiles of ichthyoliths (Fig. 6; NASC normalized) are consistent with the profiles found in a number of Paleozoic marine bioapatites (Wright et al., 1984; Grandjean et al., 1987; Wright et al., 1987; Bertram et al., 1992; Reynard et al., 1999; Kemp and Trueman, 2003) and are distinguished from the REE profile of diagenetic calcite that is flat and shows lower total REE abundances. The flat pattern is typical of shale and suggests that the enclosing sediments are the major source of REE during calcite growth. The similar shapes of the REE profiles for the bone and teeth suggest that the REE enrichment is taxon-independent and dependent only on the diagenetic environment.

5.3. Do the Nd isotopes reflect seawater? Comparison with conodonts

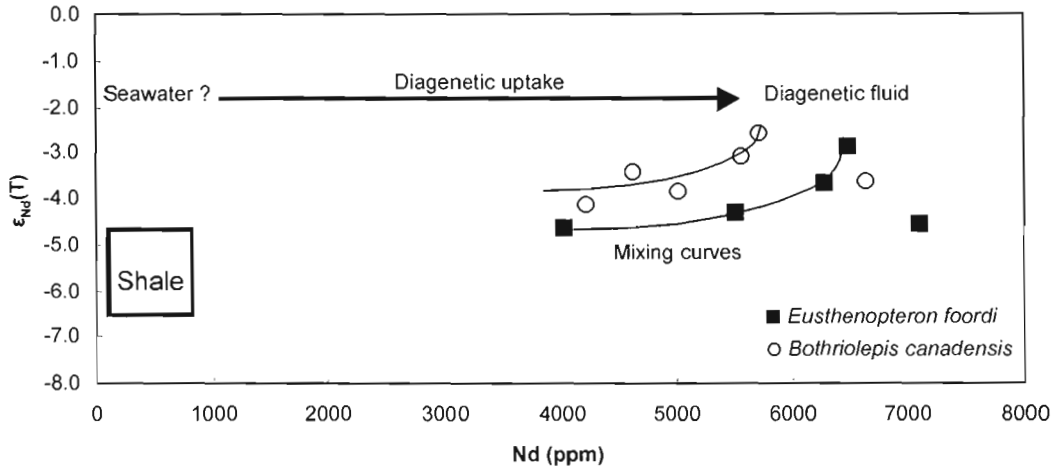
The ε_{Nd} values of the Escuminac sediments yield values comparable to other sediments shed as a result of the Taconian and Acadian orogenies (Eriksson et al., 2004; Hurowitz et al., 2005). Although there are small Nd isotopic variations within the sequence, no drastic $\varepsilon_{Nd}(T)$ shift is seen in the shales along the stratigraphic sequence (Fig. 7).

Figure 7. $\varepsilon_{Nd}(t)$ variation along the Escuminac Formation for *Bothriolepis canadensis*, *Eusthenopteron foordi* and shales. "Tooth" and "Bone" series belong to *Eusthenopteron foordi*.



This suggests that sediment sources were relatively stable throughout deposition of the Escuminac Formation and were dominated by the erosion of the young Acadian Appalachians (Hesse and Sawh, 1992; Prichonnet et al., 1996). However, the $\varepsilon_{Nd}(T)$ are more radiogenic for the Escuminac fossils (–2.6 to -4.6) than for the sediments. The difference in $\varepsilon_{Nd}(T)$ of shale and fossil material suggest the presence of at least two Nd reservoirs, one of which is Appalachian sediments and the other bearing a more radiogenic signature. Plots of $\varepsilon_{Nd}(T)$ and Nd concentration in fossil material (Fig. 8) also appear to suggest a trend that is consistent with mixing between two reservoirs; one reservoir that is less radiogenic with lower $\varepsilon_{Nd}(T)$ and low Nd concentration, and a second reservoir with higher $\varepsilon_{Nd}(T)$ and much higher Nd concentration. The high Nd content suggests that the second reservoir is the diagenetic fluid, but to what does it owe its Nd isotope composition? The fact that it is more radiogenic than the sediments suggests that the isotopic composition of the fossils reflects, at least in part, the isotopic composition of the seawater. Figure 8 illustrates that if the post-mortem REE uptake is done in equilibrium with seawater, then, the isotopic composition may be preserved.

Figure 8. Diagram showing $\varepsilon_{Nd}(T)$ values of ichthyoliths plotted against their Nd concentration. The samples differ from the shale from the Escuminac Formation. An hypothetical seawater value is presented as a possible source of REE uptake during diagenesis.

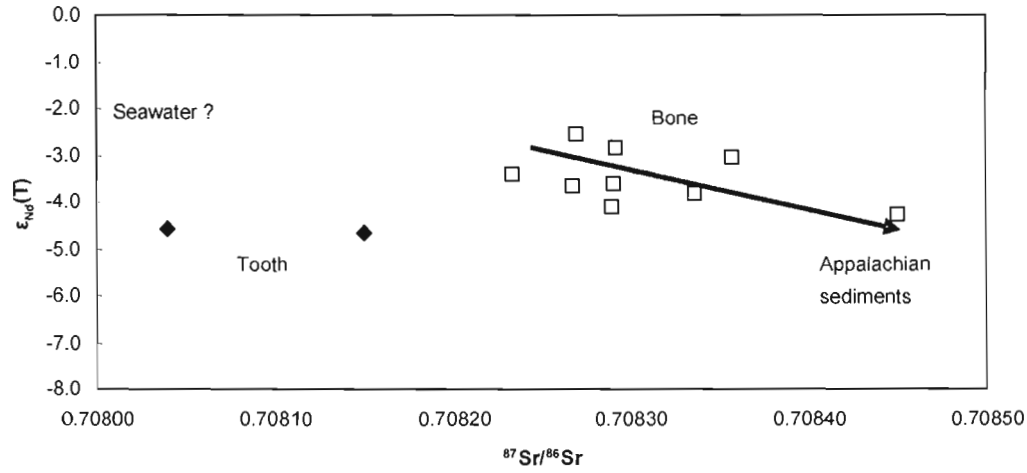


The sinusoidal variation in $\varepsilon_{Nd}(T)$ of the placoderm remains with respect to their stratigraphic position (Fig. 7) mimics that of the sediments and likely reflects the presence of sedimentary (silicate?) material that was not completely removed during cleaning. The absence of a sinusoidal pattern among the osteolepiform teeth is likely because teeth are more easily cleaned. The difference in $\varepsilon_{Nd}(T)$ between the bone and teeth is intriguing. The difference is unlikely to be due to incomplete cleaning because the placoderm fragments are more radiogenic. Could the difference in composition reflects different initial Nd isotope compositions for different species living in different water masses (e.g., pelagic vs. benthic)? Further tooth analyses are required to investigate this phenomenon.

A plot of the $\varepsilon_{Nd}(T)$ values vs $^{87}Sr/^{86}Sr$ ratios of the Miguasha fossil material (Fig. 9) also potentially shows mixing between two reservoirs, one sedimentary and the other possibly marine. The bone material of both fossil species show a broad negative correlation from high $^{143}Nd/^{144}Nd$, low $^{87}Sr/^{86}Sr$ to low $^{143}Nd/^{144}Nd$, high $^{87}Sr/^{86}Sr$. This latter component is the Appalachian sediment end of the mixing curve, whereas the high $^{143}Nd/^{144}Nd$, low $^{87}Sr/^{86}Sr$ component trends towards what may have been seawater values. The sediment contamination

may be largely owing to the presence of sediment still trapped within pores and fractures in the bones and teeth. There are only two tooth samples for which both Nd and Sr isotope data are available so there is no clear correlation on this diagram. However, the displacement of the *Eusthenopteron* teeth compared to the bony material of the same species is significant. Note that the Nd isotope compositions of the more porous bone material of *Eusthenopteron* overlap with the bone material of *Bothriolepis canadensis*.

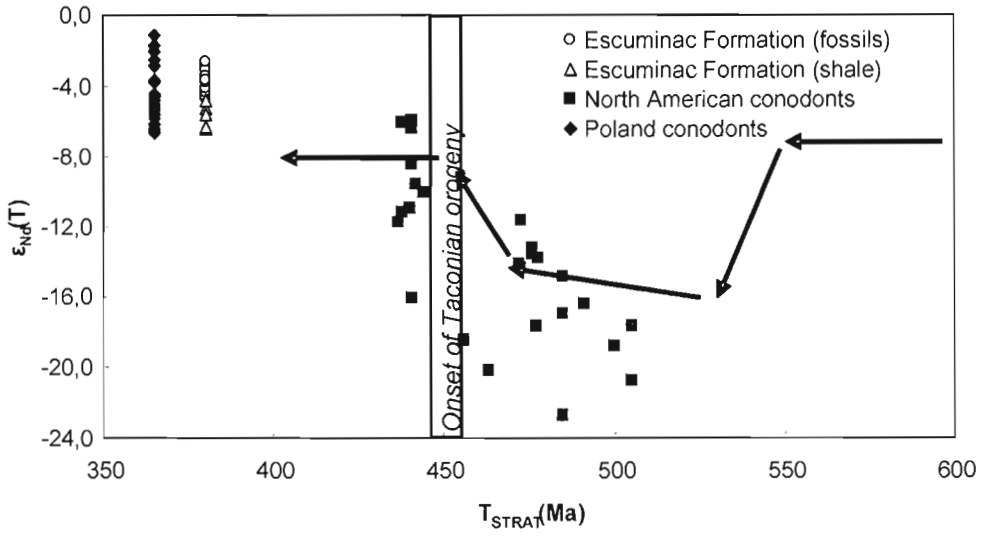
Figure 9. Sr isotope composition and $\varepsilon_{Nd}(T)$ of tooth and bone from the Escuminac Formation. Samples exhibit relatively homogeneous $\varepsilon_{Nd}(T)$ in spite of a wide range of $^{87}Sr/^{86}Sr$.



It is relevant (Fig. 10) that $\varepsilon_{Nd}(T)$ values of bioapatites from the Escuminac Formation are similar (–2.6 to -4.6) to those recorded in Late Devonian conodonts from Variscan oceanic water (-1.1 to –6.5; Dopieralska et al., 2006). This oceanic realm was situated during the Devonian between Euramerica and Gondwana and included in its western portion the Rheic Ocean, which was bordering the eastern coast of Euramerica (Dopieralska et al., 2006). The radiogenic compositions of the Miguasha ichthyoliths may, thus, represent the diagenetic fluids in isotopic equilibrium with the Rheic Ocean water. These radiogenic signatures are also consistent with the erosion of a tectonically active region such as the eastern margin of Euramerica during the Devonian. The $\varepsilon_{Nd}(T)$ values of North American conodonts are similar to those of the Miguasha sediments and post-Taconic Appalachian sediments in

general (Fig. 10). The contrastingly more radiogenic $\varepsilon_{Nd}(T)$ values of the Miguasha fossils likely reflect the difference between a restricted epieric sea that received Nd (detrital and dissolved) from both the emerging Appalachian and older exposed continental rocks, and a more open marine environment on the Rheic Ocean as represented by the Miguasha fossils that received Nd largely from orogenic terranes. Decoupling of Nd isotope compositions between epicontinental seas and bordering oceans owing to restricted water circulation has been suggested in geochemical investigations of Paleozoic bioapatites (Holmden et al., 1998; Dopieralska et al., 2006). Considering the Nd isotope compositions, fossil fishes from Miguasha have more in common with Baltic conodonts than North American conodonts. This connection is also supported by paleontological data. The Escuminac Formation ichthyofauna is considered to be closer to fish assemblages from Scottish and Baltic sequences rather than to other North American ichthyofaunas (Schultze and Cloutier, 1996) supporting the same aquatic connectivity suggested by the present study.

Figure 10. $\varepsilon_{Nd}(T)$ comparison between the material used in this study and sediments and fossils coming form other localities and periods. Black arrows represent the general trend seen in North American shales (see Hurowitz and McLennan, 2005). Data for conodonts are taken in Wright (1995; for North America) and Dopieralka et al. (2006; for Poland). Figure modified from Hurowitz and McLennan (2005).



6. CONCLUSIONS

The present study demonstrates that relevant paleoenvironmental information can be recovered through geochemical (rare earth elements) and isotopic (Rb-Sr, Nd-Sm) analyses of bioapatites and sediments from the Escuminac Formation. The main conclusions of this study are:

1. The freshwater hypothesis is not supported by Sr isotope composition of bioapatites. Although most samples show a deviation toward more freshwater ratios, some tooth material is comparable to typical Frasnian seawater $^{87}Sr/^{86}Sr$ compositions. The signatures recorded in teeth are considered more reliable than those found in more easily-altered structures such as porous bones and scales. The $^{87}Sr/^{86}Sr$ signature is more dependent on the nature of the fossil material (i.e., teeth, bone, scales) than by its stratigraphic position or its taxonomic affinity. A brackish to marine environment is suggested by $^{87}Sr/^{86}Sr$ ratios of the ichthyoliths.
2. A significant post-mortem REE uptake occured in the Miguasha fossils. This diagenetic enrichment is partially derived from the enclosing sediments, as suggested by REE patterns in diagenetic calcite and similar $\varepsilon_{Nd}(T)$ fluctuation along the Escuminac Formation for shales and *Bothriolepis* bony plates.
3. As suggested by shale $\varepsilon_{Nd}(T)$ values, the detrital sedimentation in the Escuminac Formation was dominated by sources typical of post-Taconian Appalachians.
4. Differences between shale and fossil material $\varepsilon_{Nd}(T)$ values implies the presence of at least two Nd sources for ichthyoliths, the first of them being the sediments. We suggest that a second reservoir is seawater. During diagenesis, a significant Nd uptake from seawater occurs. If this uptake is done in equilibrium with seawater, the Nd isotope composition of seawater will be preserved in ichthyoliths. This might explain the similarity observed between $\varepsilon_{Nd}(T)$ for Miguasha fossils and other Upper Devonian marine bioapatites belonging to the Variscan oceanic realm. This homogeneity between bioapatites $\varepsilon_{Nd}(T)$ values from Rheic Ocean and Miguasha implies a Rheic Ocean component within the Escuminac Formation.

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CONCLUSION

Ce travail visait à investiguer le cadre paléoenvironnemental de la Formation d'Escuminac au moyen d'analyses géochimiques (terres rares) et isotopiques (Rb-Sr, Nd-Sm) effectuées sur du matériel fossile provenant du site fossilifère de Miguasha. Les objectifs étaient d'étudier :

(1) le degré de salinité de milieu de vie des poissons fossiles;
(2) les profils de terres rares des apatites biogéniques et des sédiments;
(3) la possible variation interspécifique et stratigraphique des précédents aspects;
(4) le degré de diagénèse subit par les fossiles;
(5) la structure et la composition en éléments majeurs des bioapatites;
(6) les sources sédimentaires de la Formation d'Escuminac.

Pour ce faire, six échantillons d'argilite et 34 ichthyolithes appartenant à cinq espèces de poissons fossiles différentes (le placoderme *Bothriolepis canadensis*, l'acanthodien *Homalacanthus concinnus,* l'actinoptérygien *Cheirolepis canadensis,* le dipneuste *Scaumenacia curta* et l'ostéolépiforme *Eusthenopteron foordi*) ont été prélevés de la section type de la Formation d'Escuminac. Ces échantillons furent préparés en salles blanches puis étudiés en microscopie électronique, cartographie des rayons X, ablation laser ICP-MS et spectrométrie de masse par ionisation thermique.

Les dents et les os fossilisés, bien que renfermant des cristaux authigènes de calcite indicateurs d'une altération diagénétique, ont conservé leur minéralogie à base de phosphate de calcium. Les dents fossilisées présentent les plus faibles ratios $^{87}Sr/^{86}Sr$ obtenus dans cette étude. Ces valeurs, considérées comme les moins altérées, correspondent à une eau saumâtre à salée et suggèrent une influence marine marquée pour le paléoenvironnement de la Formation d'Escuminac. La signature $^{87}Sr/^{86}Sr$ des bioapatites semble plus influencée par la nature du matériel (i.e., dent, os, écaille) que par sa position stratigraphique ou son affinité taxonomique. Il serait hasardeux pour le moment de s'aventurer à toute considération stratigraphique ou taxonomique, tant que la comparaison n'est pas fait entre des ichthyolithes de même nature. Les shales de la Formation d'Escuminac possèdent un composition

isotopique en Nd typiques des sédiments appalachiens post-taconiens. Les bioapatites étudiées ici présentent un fort enrichissement en terres rares, qui semble en partie tributaire des sédiments encaissants. Cependant, la divergence entre la composition isotopique en Nd des shales et des fossiles suggèrent l'Influence d'un autre réservoir de Nd pour les fossiles. Ce réservoir serait une eau de mer partageant une composition isotopique similaire à celle de l'océan Rhéïque, impliquant un contact direct entre cet océan et le bassin collecteur de la Formation d'Escuminac.

Cette étude démontre que le matériel fossile de la Formation d'Escuminac se prête bien aux études géochimiques. Au terme de ce travail, plusieurs avenues de recherche n'ayant pas été explorées dans le cadre de cette maîtrise apparaissent fort intéressantes. D'abord, toute investigation s'intéressant à la récupération de signatures fidèles au milieu de vie des organismes devrait se concentrer sur le matériel dentaire, particulièrement l'émail. Il s'agit de la biominéralisation la plus résistante à l'altération diagénétique. D'autre part, toute nouvelle étude géochimique utilisant les mêmes traceurs environnementaux que ceux utilisés ici permettrait d'augmenter la résolution et la robustesse des signaux paléoenvironnementaux de la Formation d'Escuminac. Il serait particulièrement intéressant de combler les vides stratigraphiques de la présente étude afin de mieux investiguer la possible variation temporelle des signatures paléoenvironnementales. Le champ d'investigation le plus prometteur nous apparaît cependant être celui des possibles variations spatiales des signatures, avec la découverte récente de nouveaux affleurements de la Formation d'Escuminac situés jusqu'à 40 km de la section type à Miguasha. La géochimie pourrait être mis à profit au même titre que la sédimentologie, la stratigraphie, la palynologie et la paléoichthyologie dans une étude pluridisciplinaire des extensions latérales de la Formation d'Escuminac. Finalement, à plus grande échelle, il serait souhaitable que d'autres sites pertinents dans l'étude de l'émergence des tétrapodes soient étudiés et comparés à la Formation d'Escuminac. Ce faisant, une vision plus globale des variables environnementales ayant conduit à la transition de l'eau à la terre chez les vertébrés pourrait émerger.

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